

# VARIATIONS IN CHAR REACTIVITY WITH COAL TYPE AND PYROLYSIS CONDITIONS

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Understanding char reactivity is important since the consumption of char is the slowest and, therefore, the controlling process in combustion or gasification. Reviews of char reactivity (1,2) demonstrate that there is a wide variation in observed reactivities. Work described by Smoot (3) highlights the very large variations (one and half orders of magnitude) in char reactivity with method of formation. Similarly, Ashu et al. (4) found an enhanced reactivity of char caused by rapid heating of the precursor coal. More recently, in a vertical tunnel furnace, Essenhigh and Farzar (5) measured very rapid burnout times for small coal particles. They ascribed this to the firing condition which gave rates of heating in the  $10^6$  K/s regime, compared with the more usual value of  $10^4$  K/s in slower burning flames. Nsakala has reported a wide variation in reactivity associated with rank (6).

The gasification or combustion reactions of char are generally described as falling into three rate controlling regimes where the reaction rate is limited by: 1) intrinsic reactivity of the char itself, 2) diffusion of reactants within the char pores, and 3) diffusion of reactants between the char's surface and the ambient atmosphere. In this work the focus is on the intrinsic reactivity where the controlling factors are the surface area, active site density, and catalytic effect of minerals. The objective of the study described here was to determine how these factors vary with coal rank, char formation conditions and mineral matter content.

This paper reports on an empirical study of the reactivity of a set of chars from a variety of different coals prepared by pyrolysis at heating rates between 0.5 and 20,000°C/sec to temperatures between 400 and 1600°C. Reactivities were measured with a TGA, using the widely used method of monitoring the weight loss at constant temperature in the presence of  $O_2$  or  $CO_2$ . A new technique was developed in which the weight loss was measured while the sample was heated at a constant heating rate in the presence of the reactive gas. This method has the advantage that the same conditions can be used for chars of widely varying reactivity. Reactivities measured by the two methods correlated well with each other. The paper will present correlations of the reactivities with the char formation conditions and the char properties (including surface area, hydrogen concentration and mineral concentration).

## EXPERIMENTAL

**Char Preparation** - Chars for this study were prepared from the 200 x 325 mesh sieved fractions of coals and lignites listed in Table I. The chars were prepared by pyrolysis in an inert atmosphere in one of four reactors: 1) an atmospheric pressure entrained flow reactor (EFR) (7,8) with coal particle temperatures between 650 and 1600°C at heating rates of  $\sim 10,000^\circ\text{C}/\text{sec}$ ; 2) a heated tube reactor (9) with coal particle temperatures between 650°C and 950°C at heating rates of  $\sim 20,000^\circ\text{C}/\text{sec}$ ; 3) a thermogravimetric analyzer (TGA) with coal particle temperatures of 450°C to 900°C at heating rates of  $0.5^\circ\text{C}/\text{sec}$ ; and 4) a heated grid reactor (HGR) with coal temperatures of 400°C to 900°C at heating rates of  $\sim 1000^\circ\text{C}/\text{sec}$ . (10).

**Reactivity Measurements** - Initial char reactivity measurements were made using the isothermal measurement developed at Pennsylvania State University (11). In this method, the char is heated in a TGA in nitrogen to the desired temperature, usually 400-500°C. The temperature level is chosen to make sure no oxygen diffusion limitations are present, i.e., by varying the flow rate, bed depth and particle size. After the weight of the sample has stabilized at the selected temperature level, the nitrogen flow is switched to air and the weight loss is monitored. The time for 50%

burnoff,  $T_{0.5}$ , is used as the reactivity index. Another group at Penn State has used the maximum rate of weight loss as a reactivity index, which is determined in a similar isothermal experiment (12).

In our char characterization work, we had difficulty applying the isothermal techniques to chars formed over a wide range of conditions. A temperature level selected for one char was inappropriate for another. The temperature was either too high for the rate to be chemically controlled or too low for the  $T_{0.5}$  to be reached in a reasonable time period.

In order to overcome this difficulty, a non-isothermal technique was developed. A Perkin-Elmer TGA 2 was used for this method. The sample size is about 1.5 mg. The sample is heated in air at a rate of 30 K/min until a temperature of 900°C is reached. The TGA records the sample weight continuously and, at the end of the experiment, the weight and derivative are plotted. Some representative curves for the North Dakota (Zap) lignite, the Montana Rosebud subbituminous coal and the Pittsburgh Seam bituminous coal are shown in Fig. 1. The Zap and Pittsburgh were chars prepared in the (EPR), in which it was calculated that the particles were heated at about 7000 K/s to 700°C before being quenched. The Montana Rosebud char was prepared in the heated tube reactor (HTR) under similar conditions. The samples were oxidized with an air flow of 40 cc/min and a nitrogen purge flow of 40 cc/min. The Zap lignite indicates burnout of several components of the char of different reactivity, while the Rosebud and Pittsburgh coals show more homogeneous burnout at higher temperatures.

The characteristics of the weight loss curve can be understood as follows: 1) At low temperature, there is an initial weight loss as moisture is removed. 2) As the temperature is raised, the reactivity of the char increases until the fractional weight loss rate is sufficiently large to be observed. The sample size and oxygen flows are chosen so that the initial 10% of weight loss occurs under intrinsic reactivity control. 3) As the temperature continues to increase, the reactivity increases until eventually all the oxygen reaching the sample bed is consumed and the weight loss is controlled by the oxygen supply to the sample bed alone. Then the fractional weight loss rate becomes constant for all samples. 4) When the char has components of different reactivity, the weight loss can switch between being oxygen supply limited and being intrinsic reactivity limited as each component is consumed.

Figure 2 compared the weight loss curves for the same char sample but with different sample sizes. The curves are identical for the initial weight loss which is controlled by the intrinsic reactivity. As expected, the fractional rate of weight loss  $(1/m_0)(dm/dt)$  decreases with increasing sample size in the oxygen supply limited regime.

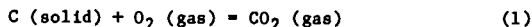
## RESULTS

**Comparison of Isothermal and Constant Heating Rate Reactivity Tests** - The temperature ( $T_{cr}$ ) at which the derivative of the fractional weight loss with respect to time reaches a value of 0.1 wt. fraction/min was chosen as an index of reactivity to be compared with the  $T_{0.5}$  values measured by the isothermal technique. The actual critical slope used is arbitrary. A value is chosen which is large enough to be unambiguously determined, but small enough so that reaction occurs in the chemically controlled regime. Values of  $\ln T_{0.5}$  were plotted against  $1/T_{cr}$  and a good correlation was observed.

It was subsequently decided that a comparison to  $T_{0.1}$  (time for 10% burnoff) would be more relevant since the initial reactivity indicated by  $T_{cr}$  would be measured, rather than an integral reactivity over a large extent of conversion which is affected by reactivity variations due to changes in the pore structure or sample

inhomogeneity. A plot of  $\ln \tau_{0.1}$  vs  $1/T_{cr}$  is shown in Fig. 3. This plot includes data for chars from all three coals in all four reactors. The experimental conditions covered the following ranges: heating rate = 0.5 to 20,000 K/sec; temperature = 400 to 1600°C; residence time = .020 s to 30 min; pressure = 0 to 200 psig.

It can be shown that a plot of  $\ln \tau_{0.1}$  vs  $1/T_{cr}$  will be linear with a slope equal to  $E/R$ , where  $E$  is the global activation energy for the intrinsic oxidation rate and  $R$  is the gas constant. For the reaction



the global rate of disappearance of carbon can be represented as follows:

$$dm/dt = -k_s C_s^n W \beta S \quad (2)$$

where  $dm/dt$  is the mass loss of carbon per particle in unit time (g/min),  $k_s$  is the intrinsic reaction rate constant based on unit surface (cm/min),  $C_s$  is the concentration of oxygen at the surface in moles/cm<sup>3</sup> raised to some power  $n$ ,  $W$  is the molecular weight of carbon in g/mole,  $\beta$  is the ratio of active area per unit accessible surface area (cm<sup>2</sup>/cm<sup>2</sup>) and  $S$  is the accessible surface area in cm<sup>2</sup> per particle. Since the reaction occurs under chemical reaction control, the concentration of oxygen at the surface will be equal to the bulk concentration, which allows one to drop the subscript.

In the isothermal experiment, the burn-off rate is nearly constant up to 10% weight loss:

$$dm/dt \approx \Delta m / \Delta t \approx -0.1 m / \tau_{0.1} \quad (3)$$

Substituting Eq. 2 for  $dm/dt$ :

$$-k_s C^n W \beta S = 0.1 m / \tau_{0.1} \quad (4)$$

$$\tau_{0.1} = \left[ 0.1 m / k_s(T_0) C^n W \right] \cdot \left[ 1 / \beta S \right] \quad (5)$$

$$= K_1 \left[ 1 / \beta S \right] \quad (6)$$

The quantities in the first set of brackets in Eq. 5 are nearly constant for a given isothermal (temperature =  $T_0$ ) experiment at low conversions and independent of coal type, while the second set of brackets contain quantities which vary with coal type and char formation conditions.

For the non-isothermal experiment, the relative rate of mass loss is constant at some critical temperature,  $T_{cr}$ :

$$\left[ 1/m \right] \cdot \left[ dm/dt \right] = -0.11 = \left[ 1/m \right] \cdot \left[ -k_s(T_{cr}) C^n W \beta S \right] \quad (7)$$

$$k_s(T_{cr}) = \left[ 0.11 m / C^n W \right] \cdot \left[ 1 / \beta S \right] \quad (8)$$

$$= K_2 \left[ 1 / \beta S \right] \quad (9)$$

The result obtained is that  $k_s$  is proportional to an experimental constant and inversely proportional to char properties.

For data collected on the same char sample, ( $\beta S$ ) can be eliminated between Eqs. 6 and 9:

$$\tau_{0.1} = \left[ K_1 / K_2 \right] k_s(T_{cr}) = \left[ 0.9 / k_s(T_0) \right] k_s(T_{cr}) \quad (10)$$

or

$$\tau_{0.1} = 0.9 \exp \left[ -E/R \left( 1/T_{cr} - 1/T_0 \right) \right] \quad (11)$$

assuming that  $k_g$  can be expressed as an Arrhenius expression  $k_g(T) = k_0 \exp(-E/RT)$ .

Consequently, a plot of  $\ln \tau_{0.1}$  vs  $1/T_{cr}$  will have a slope equal to  $-E/R$  of the intrinsic global oxidation rate. In the absence of catalytic effects, the value of  $E$  should be the same for chars from all coals and chars from the same coal prepared under a wide variety of conditions. The nearly linear data in Fig. 3 appears to support this conclusion. A problem may arise if  $T_{cr}$  and  $T_0$  are significantly different. The mechanism of the oxidation reaction probably changes with temperature, as indicated by the wide range of activation energies and reaction orders reported for the char oxidation reaction in the literature (13). The best fit value of about 35 kcal/mole determined from Fig. 3 is intermediate in reported values and close to the value of 31 kcal/mole determined by Radovic and Walker for a wide range of chars in TGA experiments (14).

In our case, the Zap lignite chars appear to fall on a line of lower slope. This is probably due to catalytic effects. When a lignite char was acid-washed, it was less reactive in the non-isothermal test. The companion isothermal test has not yet been done, so we have not yet determined where the acid-washed char falls on the plot of Fig. 3.

**Variations in Reactivity** - The reactivities were determined for a number of chars which had been prepared under carefully controlled conditions to study their pyrolysis behavior (7-11,15). Examples to illustrate the observed trends are presented in Fig. 4. Figure 4a illustrates the results for the Zap lignite. The three curves are for: 1) 150 msec with maximum temperature of 700°C (with reactivity measured in air); 2) 460 msec with maximum temperature of 1600°C (in air); 3) same as 2 but reactivity in CO<sub>2</sub>. The curves illustrate the observation that the reactivity goes down with increased exposure to high temperature (or "extent of pyrolysis") and that for the same chars, CO<sub>2</sub> reactivity is lower than oxygen reactivity. Measurements of surface area  $S$  showed that char for conditions 1 and 2 were similar, suggesting that the difference in reactivity is caused by a change in the density of active sites,  $\rho$ . Figure 4b shows results for Pittsburgh Seam coal. The three curves are for: 4) 150 msec with a maximum temperature of 700°C (in air); 5) 660 msec with a maximum temperature of 1100°C (in air) and 6) same as 5 but reactivity in CO<sub>2</sub>. For equivalent cases (1 and 4), the reactivity for the Pittsburgh Seam coal is lower than for the Zap lignite prepared under equivalent conditions. Surface area measurements show the Pittsburgh Seam coal (which melts during pyrolysis) to have about 1/4 the surface area of the Zap lignite. This difference in surface area is not sufficient to account for the differences in reactivity, however. The extra reactivity appears to result from the lignite's mineral content, but could also be due to a difference in active site densities. Figure 4c compares curve 7 for the Zap lignite with curve 8 for the demineralized coal and curve 9 for a Montana Rosebud pyrolyzed under similar conditions and having a similar surface area. Curves 8 and 9 are similar, but lower in reactivity than the raw lignite. Figure 4 illustrates the variation in reactivity with surface areas, with active site density,  $\rho$  and with mineral content.

Figure 5 summarizes the results for a number of samples. The critical temperature  $T_{cr}$  is plotted as a function of the hydrogen content which is used as a measure of the extent of pyrolysis. For each char type, there is a trend for increasing  $T_{cr}$  with decreasing hydrogen. Most of the change occurs below 2 1/2% hydrogen, after the evolution of aliphatic hydrogen is complete. That is, the  $T_{cr}$  varies primarily with the concentration of aromatic hydrogen. It should be noted that there is also ring oxygen in the char which is removed at about the same rate as the hydrogen and which may be related to the reactivity changes. This variation is due to a variation in  $\rho$  possibly correlated with the ring condensation accompanying the elimination of aromatic hydrogen.

The vertical displacement of the curves is due to the variations in char surface area and catalytic activity of the minerals. The most reactive chars are for the Zap lignite. The chars have surface areas in the neighborhood of  $200 \text{ m}^2/\text{g}$ . As pyrolysis proceeds the critical temperature  $T_{\text{cr}}$  first decreases and then increases with temperature as hydrogen is lost. There does not appear to be any drastic effects due to heating rate, as chars for a wide range of conditions all fell along the same curve. The low values of  $T_{\text{cr}}$  are believed to be due to the char's mineral content (high Na and Ca). When the coal was demineralized (symbol  $\nabla$ ),  $T_{\text{cr}}$  increased substantially. A Montana Rosebud char with a similar surface area shows a somewhat higher  $T_{\text{cr}}$  than the raw Zap.

The highest  $T_{\text{cr}}$  values are for the Pittsburgh and Kentucky coals. These swell upon pyrolysis. Initial surface area measurements of the Pittsburgh coal show approximately  $50 \text{ m}^2/\text{g}$ , suggesting that the lower surface areas are responsible for the lower reactivity. Note that the reactivity of slowly heated Pittsburgh Seam coal is higher than that of a rapidly heated char.

#### CONCLUSION

A new reactivity test has been developed which allows relative rates of reactivity to be determined for chars of widely varying reactivity. The method was applied to study the dependence of reactivity on coal properties and pyrolysis conditions. Reactivities are seen to decrease with decreasing aromatic hydrogen concentration. Reactivities were insensitive to heating rate for a lignite but were quite sensitive to heating rate for a bituminous coal. Mineral catalytic effects were also observed.

#### ACKNOWLEDGEMENT

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TABLE I

#### SAMPLE PROPERTIES

##### WT% DAF

	Zap, North Dakota Lignite	Montana Rosebud Subbituminous	Pittsburgh Seam Bituminous	Kentucky #9 Bituminous
Carbon	66.5	72.1	82.1	81.7
Hydrogen	4.8	4.9	5.6	5.6
Nitrogen	1.1	1.2	1.7	1.9
Sulfur	1.1	1.2	2.4	
Oxygen (Diff.)	26.5	20.3	8.2	
Ash (Dry Wt%)	7.1	10.0	9.2	14.1

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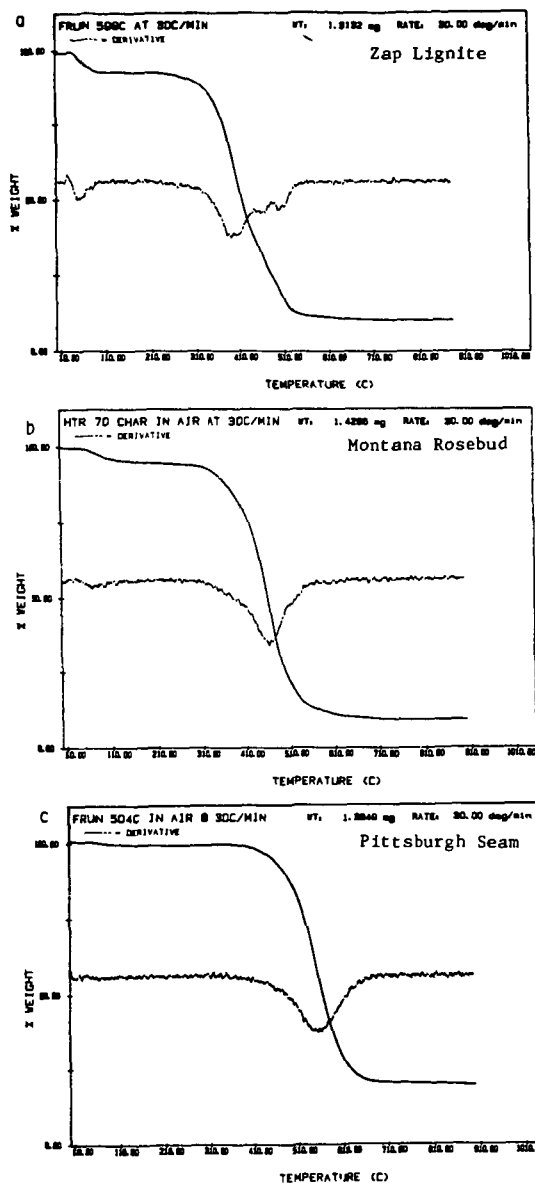


Figure 1. Non-isothermal TGA Reactivity Tests at 40 cc/min Air Flow. a) Zap Lignite, b) Montana Rosebud, and c) Pittsburgh Seam.

- ▲ Rosebud Subbituminous
- Pittsburgh Bituminous
- Zap Lignite
- ✕ Zap Demineralized

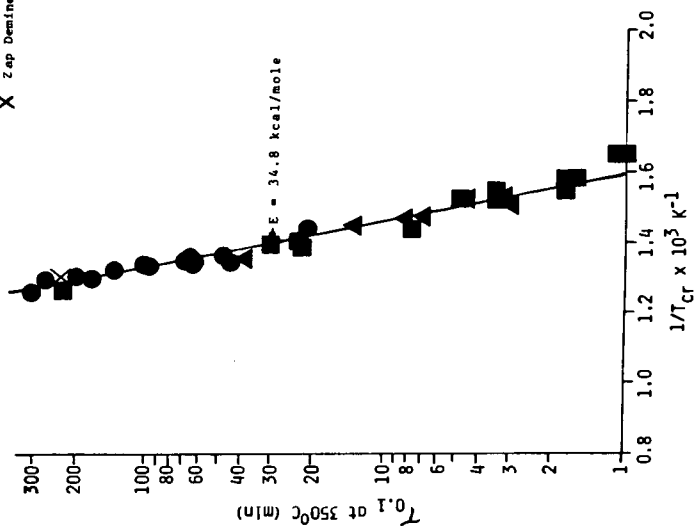


Figure 3.  $T_{0.1}$  (time for 10% burnoff) vs  $1/T_{cr}$ .  $T_{cr}$  is the Temperature at which the Weight Loss Rate Equals  $-11 \text{ wt. Fraction/min.}$

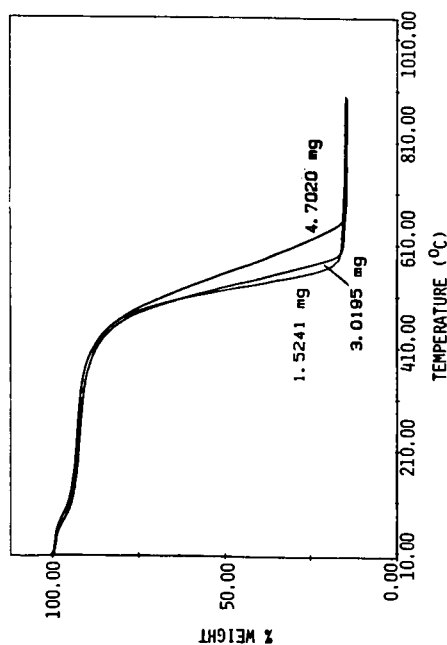


Figure 2. Comparison of Weight Loss Curves for Zap Lignite at 3 Sample Weights.



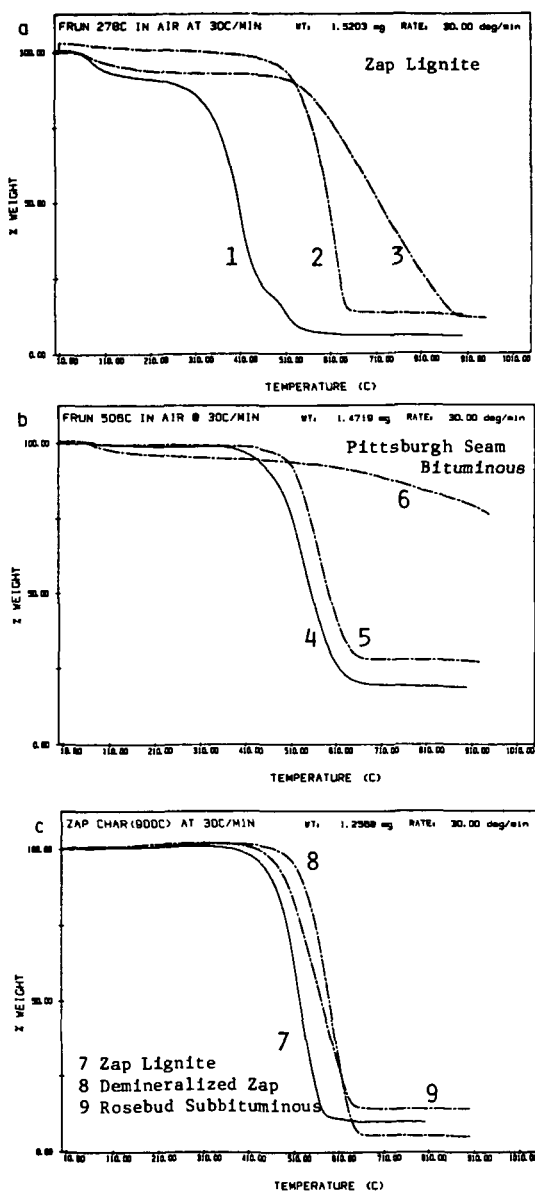


Figure 4. Comparison of Char Reactivity Curves Prepared for Three Coals Under a Variety of Conditions. Curves 3 and 6 are for Reactivity in  $\text{CO}_2$ . All the Rest are for Reactivity in Air.

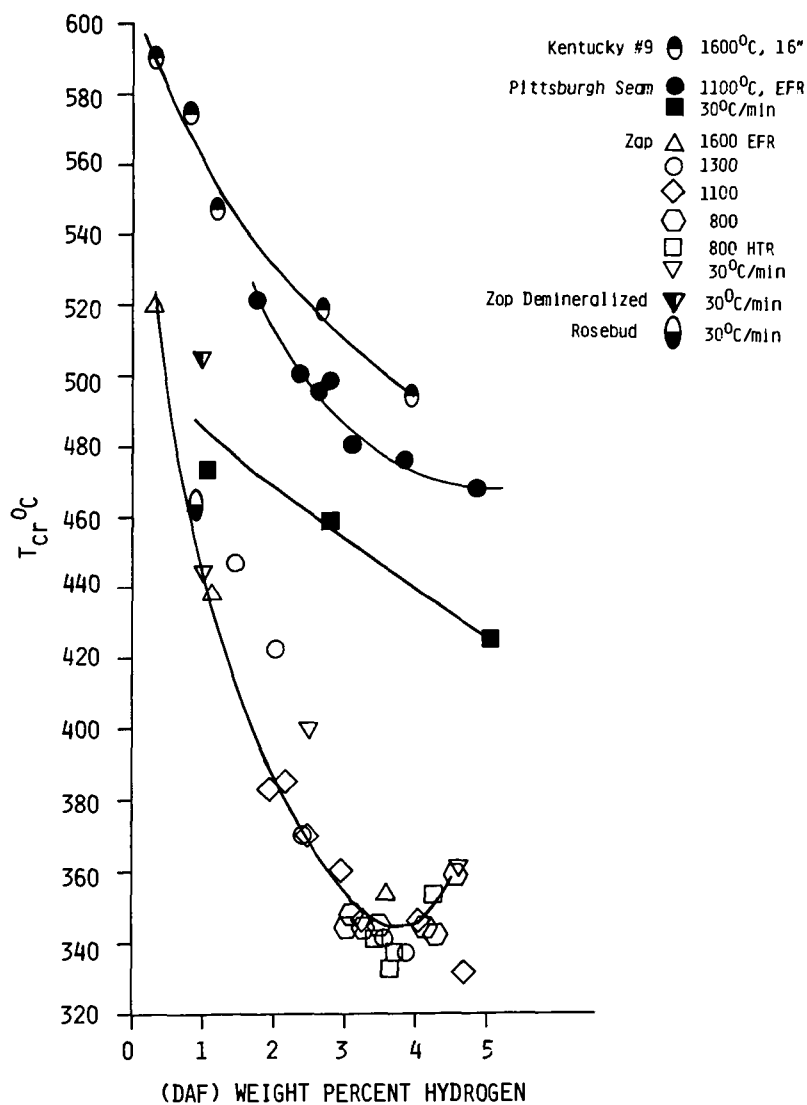


Figure 5. Variations in Reactivity with the Hydrogen Concentration in the Char (the extent of pyrolysis) and with Coal Type.